

FORM PT 1390

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

ATTORNEY DOCKET NUMBER IN-5516	U.S. APPLICATION NO. (IF KNOWN SEE P. 15) 09/914545	
INTERNATIONAL APPLICATION NO. PCT/EP00/01931	INTERNATIONAL FILING DATE 06. March 2000 (06.03.00)	PRIORITY DATE CLAIMED 06 March 1999 (06.03.99)

TITLE OF INVENTION: **SOL-GEL COATINGS FOR SINGLE-LAYER OR MULTI-LAYER VARNISHES**APPLICATION(S) FOR DO/EO/US: **Peter BETZ, Wilfried STUBBE, and Horst HINTZE-BRÜNING**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ have been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(C)(2)).
7. ☒ Amendment to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annex to the International Preliminary Examination Report under PCT Article 36

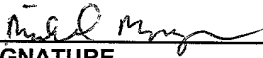
Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
13. ☒ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A Change of power of attorney and/or address letter.
16. ☒ Other items or information:

A copy of the cover sheet from the PCT Published Application
A copy of the Priority Document

I hereby certify that the attached correspondence is being deposited with the United States Postal Service in an envelope as "Express Mail Post Office to Addressee" Mailing Label No. **ET322159211US** addressed to the Commissioner for Patents, Washington, DC 20231 on August 30, 2001.


Marjorie Ellis

U.S. APPLICATION NO. 09/914545		INTERNATIONAL APPLICATION NO. PCT/EP00/01931		ATTORNEY'S DOCKET NUMBER IN-5516	
17. <input checked="" type="checkbox"/> The following fees are submitted				CALCULATIONS PTO USE ONLY	
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) Nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO.....				\$970.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO.....				\$860.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.44(a)(2)) paid to USPTO.....				\$690.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4).....				\$670.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)				\$ 96.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$860.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="text"/> 20 <input type="text"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
Claims	Number Filed	Number Extra	Rate		
Total Claims	29 - 20 =	09	X \$18.00	\$162.00	
Independent claims	01- 03 =	0	X \$80.00	\$	
Multiple dependent claims(s) (if applicable)			+ \$270.00	\$	
TOTAL OF ABOVE CALCULATION =				\$1,022.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$1,022.00	
Processing fee of \$130.00 for furnishing the English translation later the <input type="text"/> 20 <input type="text"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$1,022.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$ 40.00	
TOTAL FEES ENCLOSED =				\$1,062.00	
				Amount to be:	
				refunded	
				Charged	\$1,062.00
a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed.					
b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>23-3425</u> in the amount of <u>\$1,062.00</u> to cover the above fees A triplicate copy of this sheet is enclosed.					
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-3425</u> . A triplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: BASF CORPORATION Patent Department 26701 Telegraph Road Southfield, Michigan 48034-2442 (248) 948-2355 Customer NO. 26922			 SIGNATURE Michael F. Morgan Name 42,906 REGISTRATION NUMBER		

PATENT
(Practitioner's Docket No. IN-5516)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Peter BETZ
Wilfried STUBBE
Horst HINTZE-BRÜNING

Serial No.: This application is a National
Phase of Patent Application PCT/EP00/01931
filed 06 March 2000.

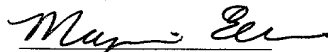
Filed: August 30, 2001

For: SOL-GEL COATINGS FOR
SINGLE-LAYER OR MULTI-LAYER
VARNISHES

Group Art Unit: Not Assigned

Examiner: Not Assigned

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Label No. **ET322159211US** addressed to BOX PATENT
APPLICATION, Commissioner for Patents, Washington,
D.C. 20231 on August 30, 2001.


Marjorie Ellis

PRELIMINARY AMENDMENT UNDER 37 CFR § 1.115

BOX PATENT APPLICATION

Commissioner for Patents
Washington, D.C. 20231

Sir:

This preliminary amendment is submitted with the application for entry into the U.S.
National Phase under Chapter II. This application is based on PCT/EP00/01931 filed on
6 March 2000.

In connection with the filing of this National Phase application, please make the
following preliminary amendments.

IN THE CLAIMS:

Please substitute claims 1-13 and 17-18 as follows. As required by 37 C.F.R. §1.121,
marked copies of the claims showing amendments for claims 1-13 and 17-18 are listed below.

Please cancel claims 14-16.

1. (Amended) A sol-gel coating material comprising
 - (A) an acrylate copolymer solution comprising a reaction product of:
 - a1) at least one (meth)acrylic ester that is substantially free of acid groups,
 - a2) at least one ethylenically unsaturated monomer that carries at least one hydroxyl group per molecule and is substantially free of acid groups, and
 - a3) at least one ethylenically unsaturated monomer that carries per molecule at least one acid group that can be converted into a corresponding acid anion group;
 - (B) a stock coating material comprising a hydrolysis and condensation product of at least one hydrolyzable silane of the general formula I



wherein:

R = hydrolyzable groups, hydroxyl groups, and nonhydrolyzable groups with the proviso that there is at least one hydrolyzable group present; and

- (C) a sol comprising a hydrolysis, condensation, and complexing product of the at least one hydrolyzable silane of the general formula I and at least one hydrolyzable metal compound of the general formula II



wherein:

M = aluminum, titanium, or zirconium,

R = hydrolyzable groups, hydroxyl groups, and nonhydrolyzable groups with the proviso that there is at least one hydrolyzable group present, and

n = 3 or 4.

2. (Amended) The sol-gel coating material of claim 1 wherein the sol-gel coating material is aromatics free.
3. (Amended) The sol-gel coating material of claim 1, wherein the sol-gel coating material comprises, based on its total amount, 5 to 40% of the acrylate copolymer solution, 5 to 40% of the stock coating material, and 1 to 15% of the sol.

4. (Amended) The sol-gel coating material of claim 1, wherein the sol-gel coating material has a solids contents of the acrylate copolymer solution (A), the stock coating material (B), and the sol (C) in a weight ratio of (A):(B):(C) of (0.5 to 5):(1 to 10):(1).
5. (Amended) The sol-gel coating material of claim 1, wherein:
the nonhydrolyzable groups R are at least one of an alkyl group; an alkenyl group; alkynyl group; and an aryl group; and
the hydrolyzable groups R are at least one of a hydrogen atom; an alkoxy group; an alkoxy-substituted alkoxy group with 3 to 20 carbon atoms; an acyloxy groups; and an alkylcarbonyl group.
6. (Amended) The sol-gel coating material of claim 5, wherein
the hydrolyzable groups R are at least one of a methoxy group, an ethoxy group, a n-propoxy group, an i-propoxy group, a n-butoxy group, a sec-butoxy group, a beta-methoxyethoxy group, an acetoxy group, a propionyloxy group, and an acetyl group; and
the nonhydrolyzable groups R are at least one of a methyl group, an ethyl group, a propyl group, a butyl group, a vinyl group, a 1-propenyl group, a 2-propenyl group, a butenyl group, an acetylenyl group, a propargyl group, phenyl, and naphthyl.
7. (Amended) The sol-gel coating material of claim 1, wherein the nonhydrolyzable group R contains at least one functional group.
8. (Amended) The sol-gel coating material of claim 1, wherein the sol is complexed by organic compounds that form chelate ligands.
9. (Amended) The sol-gel coating material of claim 1, wherein the sol-gel coating material is a sol-gel clearcoat material.
10. (Amended) A method comprising applying the sol-gel coating material of claim 1 to a substrate to produce a mar-resistant sol-gel coating.

11. (Amended) The method of claim 10, wherein the mar-resistant sol-gel coating is a cured at least one coat paint system.
12. (Amended) The method of claim 10, wherein the mar-resistant sol-gel coating is one of an automotive OEM coating, an automotive refinish coating, an industrial coating, a container coating, a plastic coating, and a furniture coating.
13. (Amended) A process comprising
- (i) applying at least one coat of a paint system to a primed or unprimed substrate,
 - (ii) applying the sol-gel coating material of claim 1 atop the paint system, and
 - (iii) curing the sol-gel coating material.
17. (Amended) A sol-gel coating comprising the sol-gel coating material of claim 1.
18. (Amended) A substrate comprising at least one sol-gel coating of claim 17.

Please insert the following new claims:

19. (New) The sol-gel coating material of claim 7, wherein the at least one functional group is at least one of an epoxide group, an amino group, an olefinically unsaturated group, a mercapto group, an isocyanate group, and a reaction product of any of the preceding with further reactive compounds.
20. (New) The sol-gel coating material of claim 1, wherein at least two of:
- the sol-gel coating material is aromatics free;
 - the sol-gel coating material comprises, based on its total amount, 5 to 40% of the acrylate copolymer solution, 5 to 40% of the stock coating material, and 1 to 15% of the sol;
 - the sol-gel coating material has a solids contents of the acrylate copolymer solution (A), the stock coating material (B), and the sol (C) in a weight ratio of (A):(B):(C) of (0.5 to 5):(1 to 10):(1);
 - the nonhydrolyzable groups R are at least one of an alkyl group; an alkenyl group; alkynyl group; and an aryl group; and the hydrolyzable groups R are at least one of a hydrogen atom; an alkoxy group; an alkoxy-substituted alkoxy group with 3 to 20 carbon atoms; an acyloxy groups; and an alkylcarbonyl group;
 - the nonhydrolyzable group R contains at least one functional group;
 - the sol is complexed by organic compounds that form chelate ligands; and
 - the sol-gel coating material is a sol-gel clearcoat material.
21. (New) The sol-gel coating material of claim 20, wherein at least one of:
- the nonhydrolyzable groups R are at least one of an alkyl group; an alkenyl group; alkynyl group; and an aryl group; and the hydrolyzable groups R are at least one of a hydrogen atom; an alkoxy group; an alkoxy-substituted alkoxy group with 3 to 20 carbon atoms; an acyloxy groups; and an alkylcarbonyl group; and
 - the at least one functional group is at least one of an epoxide group, an amino group, an olefinically unsaturated group, a mercapto group, an isocyanate

group, and a reaction product of any of the preceding with further reactive compounds.

22. (New) A sol-gel coating comprising the sol-gel coating material of claim 20.
23. (New) A substrate comprising at least one sol-gel coating of claim 22.
24. (New) A method comprising applying the sol-gel coating material of claim 20 to a substrate.
25. (New) The method of claim 13, wherein at least one of:
- the sol-gel coating material is aromatics free;
 - the sol-gel coating material comprises, based on its total amount, 5 to 40% of the acrylate copolymer solution, 5 to 40% of the stock coating material, and 1 to 15% of the sol;
 - the sol-gel coating material has a solids contents of the acrylate copolymer solution (A), the stock coating material (B), and the sol (C) in a weight ratio of (A):(B):(C) of (0.5 to 5):(1 to 10):(1);
 - the nonhydrolyzable groups R are at least one of an alkyl group; an alkenyl group; alkynyl group; and an aryl group; and the hydrolyzable groups R are at least one of a hydrogen atom; an alkoxy group; an alkoxy-substituted alkoxy group with 3 to 20 carbon atoms; an acyloxy groups; and an alkylcarbonyl group;
 - the nonhydrolyzable group R contains at least one functional group;
 - the sol is complexed by organic compounds that form chelate ligands;
 - the sol-gel coating material is a sol-gel clearcoat material;
 - the applied sol-gel coating material is cured by irradiation with intermediate IR radiation;
 - the at least one coat paint system has been completely cured; and
 - the at least one coat paint system is one of an automotive OEM coating, an automotive refinish coating, an industrial coating, a container coating, a plastic coating, and a furniture coating.

26. (New) The method of claim 25, wherein at least one of:
- a. the nonhydrolyzable groups R are at least one of an alkyl group; an alkenyl group; alkynyl group; and an aryl group; and the hydrolyzable groups R are at least one of a hydrogen atom; an alkoxy group; an alkoxy-substituted alkoxy group with 3 to 20 carbon atoms; an acyloxy groups; and an alkylcarbonyl group; and
 - b. the at least one functional group is at least one of an epoxide group, an amino group, an olefinically unsaturated group, a mercapto group, an isocyanate group, and a reaction product of any of the preceding with further reactive compounds.
27. (New) A sol-gel coating material produced by the process of claim 13.
28. (New) A substrate comprising at least one sol-gel coating of claim 27.
29. (New) A sol-gel coating material produced by the process of claim 25.
30. (New) A substrate comprising at least one sol-gel coating of claim 29.
31. (New) A sol-gel coating material produced by the process of claim 26.
32. (New) A substrate comprising at least one sol-gel coating of claim 31.

Version with Markings to Show Changes Made

As is permitted by 37 C.F.R. §1.121(c)(1)(ii), amendments to the claims are shown by an equivalent marking system. Insertions are still shown by underline, and deletions are shown by strikethrough.

1. (Amended) A sol-gel coating material comprising
- (A) an acrylate copolymer solution comprising ~~at least one acrylate copolymer~~ (A1) ~~preparable by copolymerizing at least the following monomers~~ a reaction product of:
- a1) at least one (meth)acrylic ester ~~which~~that is substantially free of acid groups,
- a2) at least one ethylenically unsaturated monomer ~~which~~that ~~bears~~carries at least one hydroxyl group per molecule and is substantially free of acid groups, and
- a3) at least one ethylenically unsaturated monomer ~~which bears~~that carries per molecule at least one acid group ~~which is convertible~~that can be converted into the a corresponding acid anion group;
- (B) a stock coating material ~~preparable by hydrolyzing and condensing~~comprising a hydrolysis and condensation product of at least one hydrolyzable silane (B1) of the general formula I



~~wherein the variable R has the following meaning:~~

R = hydrolyzable groups, hydroxyl groups, and nonhydrolyzable groups with the proviso that there is at least one ~~and there are preferably at least two~~ hydrolyzable group(s) present; and

- (C) a sol ~~preparable by hydrolyzing, condensing and complexing~~comprising a hydrolysis, condensation, and complexing product of the at least one hydrolyzable silane (B1) of the general formula I and at least one hydrolyzable metal compound (C1) of the general formula II



~~where the variables and the index have the following meaning~~wherein:

M = aluminum, titanium, or zirconium,

R = hydrolyzable groups, hydroxyl groups, and nonhydrolyzable groups with the proviso that there is at least one and there are preferably at least two hydrolyzable group(s) present, and

n = 3 or 4.

2. (Amended) The sol-gel coating material of claim 1 ~~characterized in that it~~wherein the sol-gel coating material is aromatics free.
3. (Amended) The sol-gel coating material of claim 1 ~~or 2, characterized in that it~~wherein the sol-gel coating material comprises, ~~in each case based on its total amount, 5 to 40, preferably 10 to 35 and especially 15 to 30 weight % of the acrylate copolymer solution (A), 5 to 40, preferably 10 to 35 and especially 15 to 30 weight % of the stock coating material, (B) and also 1 to 15, preferably 2 to 10 and especially 3 to 8 weight % of the sol (C).~~
4. (Amended) The sol-gel coating material of ~~any of claims 1 to 3, characterized in that wherein the sol-gel coating material has a~~ solids contents of the constituents acrylate copolymer solution (A), the stock coating material (B), and the sol (C) are in a weight ratio of (A):(B):(C) of
———(0.5 to 5):(1 to 10):(1),
preferably 1 to 4:2 to 8:1 and
especially 1.5 to 3:3 to 6:1.
5. (Amended) The sol-gel coating material of ~~any of claims 1 to 4, characterized in that wherein:~~
———the nonhydrolyzable groups R are at least one of an alkyl groups, especially of 1 to 4 carbon atoms; an alkenyl groups, especially of 2 to 4 carbon atoms; alkynyl groups, especially of 2 to 4 carbon atoms; and/or an aryl groups, especially of 6 to 10 carbon atoms; and
———the hydrolyzable groups R are at least one of a hydrogen atoms; an alkoxy groups, especially of 1 to 20 carbon atoms; an alkoxy-substituted alkoxy groups of with 3 to 20 carbon atoms; an acyloxy groups, especially of 1 to 4 carbon atoms; and an alkylcarbonyl groups, especially of 2 to 6 carbon atoms.

6. (Amended) The sol-gel coating material of claim 5, ~~characterized in that~~ wherein ~~the hydrolyzable groups R are at least one of a methoxy group, an ethoxy group, a n-propoxy group, an i-propoxy group, a n-butoxy group, a sec-butoxy group, a beta-methoxyethoxy group, an acetoxy group, a propionyloxy group, and/or an acetyl groups; and~~
the ~~—~~nonhydrolyzable groups R are at least one of a methyl group, an ethyl group, a propyl group, a butyl group, a vinyl group, a 1-propenyl group, a 2-propenyl group, a butenyl group, an acetylenyl group, a propargyl group, phenyl, and/or naphthyl groups.
7. (Amended) The sol-gel coating material of ~~any of claims 1 to 6, characterized in that~~ wherein the nonhydrolyzable groups R contains at least one functional group, ~~especially at least one epoxide group, amino group, olefinically unsaturated group, mercapto group and/or isocyanate group and/or their reaction products with further reactive compounds.~~
8. (Amended) The sol-gel coating material of ~~any of claims 1 to 7, characterized in that~~ wherein the sol is complexed by ~~complexing is effected using organic compounds which that~~ form chelate ligands.
9. (Amended) The sol-gel coating material of ~~any of claims 1 to 8, characterized in that~~ wherein it the sol-gel coating material is a sol-gel clearcoat material.
10. (Amended) ~~The use of~~ A method comprising applying the sol-gel coating material of ~~any of claims 1 to 9 to a substrate to produce a for producing mar-resistant sol-gel coatings, especially for single coat or multicoat paint systems.~~
11. (Amended) ~~The use of the sol-gel coating material~~ method of claim 10, ~~characterized in that~~ wherein the mar-resistant sol-gel coating is a cured single coat or multicoat at least one coat paint systems are concerned.
12. (Amended) ~~The use of the sol-gel coating material~~ method of claim 10 or 11, ~~characterized in that the paint systems are~~ wherein the mar-resistant sol-gel coating is

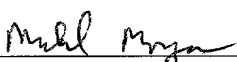
one of vehicle original equipment manufacturing coatings, vehicle repair coatings, an automotive OEM coating, an automotive refinish coating, an industrial coatings, including a container coatings, a plastics coatings, and a furniture coatings.

13. (Amended) A process for ~~producing mar-resistant sol-gel coatings on single-coat or multicoat paint systems by~~comprising
- (i) ~~applying a single-coat or multicoat~~at least one coat of a paint system to a primed or unprimed substrate,
 - (ii) ~~applying a~~the sol-gel coating material of claim 1 atop the ~~single-coat or multicoat paint system,~~ and
 - (iii) curing the sol-gel coating material;
- ~~characterized in that a sol-gel coating material as claimed in any of claims 1 to 9 is used.~~
17. (Amended) A ~~S~~sol-gel coatings ~~preparable from a sol-gel coating material as claimed in any~~comprising the sol-gel coating material of claims 1 to 9 and/or by the process of any of claims 13 to 16.
18. (Amended) A ~~S~~substrates comprising at least one sol-gel coating ~~as claimed in~~of claim ~~18~~17.

REMARKS

Upon entry of the present amendment claims 1-13 and 17-32 are pending in the application. Claims 1-13 and 17-18 have been amended in accordance with the requirements of U.S. patent practice. New claims 19-32 add no new matter, as these claims contain subject matter deleted from the amended claims. There is 1 independent claim and a total of 29 claims pending in the application. Applicants respectfully request entry of the preliminary amendment.

Respectfully Submitted,



Michael F. Morgan
Registration No. 42,906
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(248)-948-2355

WO 00/53687

PCT/EP00/01931

**Sol-gel coating for single-coat or multicoat paint
systems**

The present invention relates to a novel sol-gel
5 coating material for producing sol-gel coatings atop
single-coat or multicoat paint systems. The present
invention relates in particular to a novel process for
producing coated substrates, especially coated
automobile bodies, by initially providing the
10 substrates with a multicoat paint system and then
applying a sol-gel coating material thereatop and
curing it.

Automobile bodies are for the most part provided with a
15 multicoat coating system. As the final coat, it is
common to apply clearcoat materials. Useful clearcoat
materials include the customary and known one
component, two component, multicomponent (three
component, four component) powder or powder slurry
20 clearcoat materials or UV curable clearcoat materials.

One component, two component or multicomponent (three
component, four component) clearcoat materials are
described for example in the patent documents
25 US-A-5,474,811, US-A-5,356,669, US-A-5,605,965,
WO 94/10211, WO 94/10212, WO 94/10213, EP-A-0 594 068,
EP-A-0 594 071, EP-A-0 594 142, EP-A-0 604 992,
WO 94/222969, EP-A-0 596 460 or WO 92/22615.

T00230-5454560

Powder clearcoat materials are known for example from German patent document DE-A-42 22 194 or BSF Lacke + Farben AG's 1990 Pulverlacke product bulletin.

5 Powder slurry coatings are powder coatings in the form of aqueous dispersions. Slurries of this kind are described for example in the US patent US-A-4,268,542 and the German patent applications DE-A-195 18 392.4 and DE-A-196 13 547 and the German patent application
10 DE-A-198 14 471.7, which was unpublished at the priority date of the present invention.

UV curable clearcoat materials are disclosed for example in the patent documents EP-A-0 540 884,
15 EP-A-0 568 967 or US-A-4,675,234.

Each of these clearcoat materials has specific strengths and weaknesses. They do provide multicoat paint systems meeting the optical requirements. Yet the
20 mar-resistant one component clearcoat materials are occasionally not sufficiently weathering resistant, whereas the weathering resistant two component or multicomponent (three component, four component) clearcoat materials are frequently insufficiently mar
25 resistant. Some one component clearcoat materials are mar resistant and stable to weathering, but combined with frequently employed waterborne basecoat materials give rise to surface defects such as wrinkling.

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Powder clearcoat materials, powder slurry clearcoat materials and UV curable clearcoat materials, by contrast, possess an unsatisfactory intercoat adhesion without wishing to imply that the mar resistance or
5 etch resistance problems are completely solved.

Recently, materials known as sol-gel clearcoats and based on siloxane-containing coating formulations have been developed which are obtained by hydrolysis and
10 condensation of silane compounds. These coating materials, which are used as coating compositions on plastics, are described for example in the German patent documents DE-A-43 03 570, 34 07 087, 40 11 045, 40 25 215, 38 28 098, 40 20 316 or 41 22 743.

15 Sol-gel clearcoats impart very good mar resistance to substrates made of plastic, such as spectacle lenses or motorcycle helmet visors, for example. This mar resistance is not achieved by the known OEM (original
20 equipment manufacturing) clearcoat materials normally used for the original finishing of vehicles. The automotive industry is now demanding that this improved mar resistance be transferred to the clearcoat materials used in the finishing of automobiles as well.

25 Replacing the OEM clearcoat materials or OEM powder slurry clearcoat materials commonly used in automotive finishing by sol-gel clearcoat materials is not a straightforward matter, however, since the sol-gel

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clearcoats are too brittle for this purpose, for example, or since the attempt to conform them to the OEM requirements frequently provides only poor optical properties (appearance). Above all, the sol-gel
5 clearcoat materials are too expensive. The economically more favorable use of the sol-gel clearcoat materials as an additional coat over the clearcoats or powder slurry clearcoats used to date gives rise to adhesion problems between the clearcoat and the sol-gel coat,
10 these problems arising in particular after stone chipping and on exposure to condensation.

These problems can be solved by curing the clearcoat which is to be coated with the sol-gel clearcoat only
15 partially, so that the sol-gel coat can be chemically anchored as it were on the clearcoat in the course of the conjoint curing. However, this approach would require that, on one and the same coating line, the clearcoats on automobile bodies which are to be
20 overcoated have to be cured at a different temperature than the clearcoats of the other automobile bodies which are not to be overcoated. The use of different curing conditions on one and the same coating line constitutes a substantial disadvantage. This
25 disadvantage is additionally aggravated by the fact that the second layer of clearcoat material requires a long oven drying time to cure.

It is an object of the present invention to provide a

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novel sol-gel coating material whereby the advantageous properties of the sol-gel coatings are combinable with the advantageous properties of the known single-coat or multicoat paint systems, especially the multicoat paint systems for automotive DEM coating, without any need for departures from the customarily employed coating process, especially the wet on wet process of automotive OEM coating. In other words, the novel sol-gel coating material shall permit the subsequent application, within a short time, of a mar resistant coating atop ready produced, previously cured paint systems without any adhesion problems arising in the process.

This object is achieved by the novel sol-gel coating material comprising

(A) an acrylate copolymer solution comprising at least one acrylate copolymer (A1) preparable by copolymerizing at least the following monomers:

a1) at least one (meth)acrylic ester which is substantially free of acid groups,

a2) at least one ethylenically unsaturated monomer which bears at least one hydroxyl group per molecule and is substantially free of acid groups, and

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characterized in that a subject coating material is used.

In what follows, the novel process for producing sol-gel coatings atop single-coat or multicoat paint systems will be referred to as the subject process for brevity.

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The invention further provides novel sol-gel coatings which are preparable from the subject coating materials and will hereinafter be referred to as the subject sol-gel coatings.

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Not least the invention provides novel substrates which comprise at least one subject sol-gel coating and will hereinafter be referred to as the subject substrates.

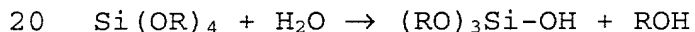
15 In the light of the background art, it is surprising and unforeseeable for one skilled in the art that the object underlying the invention is accomplished by the subject coating material and the subject process. It is especially surprising that the subject coating material
20 should readily adhere to the ready produced, cured paint systems without detachments or cracks occurring on stone chipping or following exposure to condensation, i.e., ten days' exposure of the coats in an atmosphere of 40°C and 100% relative humidity.
25 Moreover, the optical properties of the paint systems provided with the subject sol-gel coatings meet all requirements.

The subject coating material is a siloxane-containing

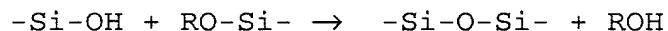
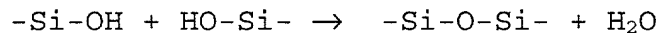
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- coating formulation which can be prepared by reacting hydrolyzable silicon compounds with water or water-detaching agents and which contains organic constituents to improve certain properties. A general
- 5 description of such systems may be found for example in the article by Bruce M. Novak, "Hybrid Nanocomposite Materials - Between Inorganic Glasses and Organic Polymers", in Advanced Materials, 1993, 5, No. 6, pages 422-433, or in the contribution of R. Kasemann,
- 10 H. Schmidt to the 15th International Conference, International Centre for Coatings Technology, Paper 7, "Coatings for mechanical and chemical protection based on organic-inorganic Sol-Gel Nanocomposites", 1993.
- 15 The basic reactions take place in a sol-gel process in which tetraorthosilicates are hydrolyzed and condensed in the presence or absence of a cosolvent:

Hydrolysis:



Condensation:



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in which R may be alkyl, such as methyl or ethyl. Tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS) are frequently used. The reactions are catalyzed using acids, bases or fluoride ions.

The subject coating material accordingly comprises siloxane-containing structures modified by organic constituents (Ormocer® = Organically Modified Ceramic).

5 The subject sol-gel coating is produced by controlled hydrolysis and condensation of silicate esters and of metal alkoxides. Specific properties are conferred on the subject sol-gel coating through the incorporation into the silicatic network of organically modified
10 silica derivatives. They allow the construction of an organic polymer network in addition to the basic inorganic scaffold when organic radicals are used which preferably contain olefinically unsaturated groups and/or epoxide groups.

15 The modifying can be effected for example by having a ready produced organic polymer present during the hydrolysis and condensation of the starting materials or in the sol.

20 The subject coating material consists of the three essential components (A), (B) and (C).

Component (A) is an acrylate polymer solution. It is
25 preferably free of aromatic solvents.

For the purposes of the present invention, the expression "free of aromatic solvents" or "aromatics free" is to be understood here and hereinbelow as

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meaning that the level of aromatic solvents or aromatic compounds in a solution is <1 weight %, preferably <0.5 weight % and particularly preferably <0.2 weight % and is especially below the limit of detection by gas chromatography.

The acrylate polymer solution (A) to be used according to the invention contains at least one acrylate copolymer (A1) which is prepared by a copolymerization of the hereinbelow specified monomers (a1), (a2) and (a3) and optionally further monomers (a4), (a5) and/or (a6) wherein (a1), (a2) and (a3) and also optionally (a4), (a5) and (a6) are chosen in terms of type and amount in such a way that the acrylate copolymer (A1) has the desired OH number, acid number and molecular weight. The acrylate polymers (A1) preferably have a hydroxyl number of 40 to 240, particularly preferably 60 to 210 and especially 100 to 200, an acid number of 5 to 100, particularly preferably 10 to 60 and especially 20 to 40, glass transition temperatures of -35 to +85°C and number average molecular weights Mn of 1 000 to 300 000.

The polyacrylate resins used inventively may be prepared using as monomer (a1) any (meth)acrylic acid alkyl or cycloalkyl ester which is copolymerizable with (a2), (a3), (a4), (a5) and (a6) and has up to 20 carbon atoms in the alkyl radical, especially methyl, ethyl, propyl, n-butyl, sec-butyl, tert-butyl, hexyl,

enically unsaturated carboxylic acid which is derived from an alkylene glycol which is esterified with the acid or are obtainable by reacting the acid with an alkylene oxide; especially hydroxyalkyl esters of

5 acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid or itaconic acid, in which the hydroxyalkyl group contains up to 20 carbon atoms, such as 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 3-hydroxybutyl, 4-hydroxybutyl

10 acrylate, methacrylate, ethacrylate, crotonate, maleate, fumarate or itaconate; 1,4-bis(hydroxymethyl)cyclohexane, octahydro-4,7-methano-1H-indenedimethanol or methylpropanediol monoacrylate, monomethacrylate, monoethacrylate, monocrotonate, monomaleate, monofumarate or monoitaconate; or reaction

15 products of cyclic esters, such as epsilon-caprolactone, for example, and these hydroxyalkyl esters; or olefinically unsaturated alcohols such as allyl alcohol or polyols such as trimethylolpropane

20 monoallyl or diallyl ether or pentaerythritol monoallyl, diallyl or triallyl ether. As far as these higher-functional monomers (a2) are concerned, the comments made for the higher-functional monomers (a1) apply analogously. The proportion of trimethylolpropane

25 monoallyl ether is usually from 2 to 10 weight %, based on the overall weight of the monomers (a1) to (a6) used to prepare the polyacrylate resin. In addition, however, it is also possible to add from 2 to 10% by weight, based on the overall weight of the monomers

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As the monomer (a4) it is possible to use one or more vinyl esters of alpha-branched monocarboxylic acids having 5 to 18 carbon atoms in the molecule. The

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carbon atom can take place before, during or after the polymerization reaction. As the component (a5) it is preferred to use the reaction product of acrylic acid and/or methacrylic acid with the glycidyl ester of Versatic acid. This glycidyl ester is commercially available under the name "Cardura E10".

As the monomer (a6) it is possible to use all ethylenically unsaturated monomers, or mixtures of such monomers, which are copolymerizable with (a1), (a2), (a3), (a4) and (a5), are different from (a1), (a2), (a3) and (a4), and are substantially free from acid groups. Suitable components (a6) include the following:

- 15 - olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, cyclohexene, cyclopentene, norbornene, butadiene, isoprene, cyclopentadiene and/or dicyclopentadiene;
- 20 - (meth)acrylamides such as (meth)acrylamide, N-methyl-, N,N-dimethyl-, N-ethyl-, N,N-diethyl-, N-propyl-, N,N-dipropyl-, N-butyl-, N,N-dibutyl-, N-cyclohexyl- and/or N,N-cyclohexylmethyl(meth)-acrylamide;
- 25 - monomers containing epoxide groups, such as the glycidyl ester of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid and/or itaconic acid;

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- vinylaromatic hydrocarbons, such as styrene, alpha-alkylstyrenes, especially alpha-methylstyrene, and/or vinyltoluene;
- 5 - nitriles such as acrylonitrile and/or methacrylonitrile;
- vinyl compounds such as vinyl chloride, vinyl fluoride, vinylidene dichloride, vinylidene difluoride; N-vinylpyrrolidone; vinyl ethers such
10 as ethyl vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether and/or vinyl cyclohexyl ether; vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl pivalate and/or
15 the vinyl ester of 2-methyl-2-ethylheptanoic acid; and/or
- polysiloxane macromonomers having a number-average
20 molecular weight Mn of from 1 000 to 40 000, preferably from 2 000 to 20 000, with particular preference from 2 500 to 10 000 and in particular from 3 000 to 7 000 and having on average from 0.5 to 2.5, preferably from 0.5 to 1.5, ethylenically
25 unsaturated double bonds per molecule, as described in DE-A-38 07 571 on pages 5 to 7, in DE-A-37 06 095 in columns 3 to 7, in EP-B-0 358 153 on pages 3 to 6, in US-A-4,754,014 in columns 5 to 9, in DE-A-44 21 823 or in the

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(a5) from 0 to 25% by weight of the component (a5), and

the sum of the weight fractions of the components (a1)
5 to (a6) being 100% in each case.

15 Examples of suitable polymerization initiators are
initiators which form free radicals, such as, for
example, tert-butyl peroxyethylhexanoate, benzoyl
peroxide, di-tert-amyl peroxide, azobisisobutyro-
nitrile, and tert-butyl perbenzoate. The initiators are
20 used preferably in an amount of from 1 to 25% by
weight, with particular preference from 2 to 10% by
weight, based on the overall weight of the monomers.

Preferred solvents used are ethoxyethyl propionate and isopropoxypropanol.

The acrylate copolymer (A1) is preferably prepared by a two-stage process since the resulting subject coating materials have a better processability. Preferred acrylate copolymers (A1) are therefore obtainable by

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1. polymerizing a mixture of the monomers (a1) and (a2) and, if desired, (a4), (a5) and/or (a6), or a mixture of portions of the monomers (a1) and (a2) and also, if desired, (a4), (a5) and/or (a6), in an organic solvent, and

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2. after at least 60% by weight of the mixture of (a1) and (a2) and, if desired, (a4), (a5) and/or (a6) have been added, adding the monomer (a3) and any remainder of the monomers (a1) and (a2) and, if appropriate, (a4), (a5) and/or (a6), and continuing polymerization.

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In addition, however, it is also possible to include the monomers (a4) and/or (a5) in the initial charge, together with at least some of the solvent, and to meter in the remaining monomers. Furthermore, it is also possible for only some of the monomers (a4) and/or (a5) to be included in the initial charge, together with at least some of the solvent, and for the remainder of these monomers to be added as described above. Preferably, for example, at least 20% by weight of the solvent and about 10% by weight of the monomers (a4) and (a5), and, if desired, portions of the

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monomers (a1) and (a6), are included in the initial charge.

Preference is further given to a two-stage process for the preparation of the inventively used acrylate polymers (A1) in which the first stage lasts for from 1 to 8 hours, preferably from 1.5 to 4 hours, and the mixture of (a3) and any remainder of the monomers (a1), (a2) and, if appropriate, (a4), (a5) and (a6) is added over the course of from 20 to 120 minutes, preferably over the course of from 30 to 90 minutes. Following the end of the addition of the mixture of (a3) and any remainder of the monomers (a1) and (a2) and, if appropriate, (a4), (a5) and (a6) polymerization is continued until all of the monomers used have undergone substantially complete reaction. In this case, the second stage may follow on immediately from the first. Alternatively, the second stage may be commenced only after a certain time, for example, after from 10 minutes to 10 hours.

The amount, and rate of addition, of the initiator is preferably chosen so as to give an acrylate copolymer (A1) having a number-average molecular weight M_n of from 1 000 to 30 000 daltons. It is preferred to commence the addition of initiator some time, generally from about 1 to 15 minutes, before the addition of the monomers. Furthermore, preference is given to a process in which the addition of initiator is commenced at the

same point in time as the addition of the monomers and ended about half an hour after the addition of the monomers has ended. The initiator is preferably added in a constant amount per unit time. Following the end
5 of the addition of initiator, the reaction mixture is held at polymerization temperature (generally 1.5 hours) until all of the monomers used have undergone substantially complete reaction. "Substantially complete reaction" is intended to denote that
10 preferably 100% by weight of the monomers used have been reacted but that it is also possible for a small residual monomer content of not more than up to about 0.5% by weight, based on the weight of the reaction mixture, to remain unreacted.

15 Preferably, the monomers for preparing the acrylate copolymers (A1) are polymerized with not too high a polymerization solids, preferably with a polymerization solids of from 80 to 50% by weight, based on the
20 monomers, and then the solvents are partially removed by distillation, so that the resulting acrylate copolymer solutions (A1) have a solids content of preferably from 100 to 60% by weight.

25 For use in the subject coating material, the solids content of the acrylate copolymer solutions (A1) is adjusted with at least one aromatics-free solvent to less than 60% by weight, preferably less than 40% by weight, and in particular less than 30% by weight.

Examples of suitable solvents are ethoxyethyl propionate and butyl glycol.

The preparation of the acrylate copolymers (A1) for
5 inventive use has no special features in terms of
method but instead takes place with the aid of the
methods which are customary and known in the field of
polymers for continuous or batchwise copolymerization
under atmospheric or superatmospheric pressure in
10 stirred vessels, autoclaves, tube reactors or Taylor
reactors.

Examples of suitable copolymerization processes are
described in the patents DE-A-197 09 465, DE-C-197 09 476,
15 DE-A-28 48 906, DE-A-195 24 182, EP-A-0 554 783, WO
95/27742 or WO 82/02387.

In accordance with the invention, Taylor reactors are
advantageous.

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Taylor reactors, which serve to convert substances
under the conditions of Taylor vortex flow, are known.
They consist essentially of two coaxial concentric
cylinders of which the outer is fixed while the inner
25 rotates. The reaction space is the volume formed by the
gap between the cylinders. Increasing angular velocity
 ω_i of the inner cylinder is accompanied by a series of
different flow patterns which are characterized by a
dimensionless parameter, known as the Taylor number Ta .

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As well as the angular velocity of the stirrer, the Taylor number is also dependent on the kinematic viscosity ν of the fluid in the gap and on the geometric parameters, the external radius of the inner cylinder r_i , the internal radius of the outer cylinder r_o and the gap width d , the difference between the two radii, in accordance with the following formula:

$$Ta = \omega_i r_i d \nu^{-1} (d/r_i)^{1/2} \quad (I)$$

where $d = r_o - r_i$.

At low angular viscosity, the laminar Couette flow, a simple shear flow, develops. If the rotary speed of the inner cylinder is increased further, then, above a critical level, alternately contrarotating vortices (rotating in opposition) occur, with axes along the peripheral direction. These vortices, called Taylor vortices, are rotationally symmetric and have a diameter which is approximately the same size as the gap width. Two adjacent vortices form a vortex pair or a vortex cell.

The basis of this behavior is the fact that, in the course of rotation of the inner cylinder with the outer cylinder at rest, the fluid particles that are near to the inner cylinder are subject to a greater centrifugal force than those at a greater distance from the inner cylinder. This difference in the acting centrifugal forces displaces the fluid particles from the inner to

the outer cylinder. The centrifugal force acts counter to the viscosity force, since for the motion of the fluid particles it is necessary to overcome the friction. If there is an increase in the rotary speed, there is also an increase in the centrifugal force. The Taylor vortices are formed when the centrifugal force exceeds the stabilizing viscosity force.

In the case of Taylor flow with a low axial flow, each vortex pair passes through the gap, with only a low level of mass transfer between adjacent vortex pairs. Mixing within such vortex pairs is very high, whereas axial mixing beyond the pair boundaries is very low. A vortex pair may therefore be regarded as a stirred tank in which there is thorough mixing. Consequently, the flow system behaves as an ideal flow tube in that the vortex pairs pass through the gap with constant residence time, like ideal stirred tanks.

Of advantage in accordance with the invention here are Taylor reactors having an external reactor wall located within which there is a concentrically or eccentrically disposed rotor, a reactor floor and a reactor lid, which together define the annular reactor volume, at least one means for metered addition of reactants, and a means for the discharge of product, where the reactor wall and/or the rotor are or is geometrically designed in such a way that the conditions for Taylor vortex flow are met over substantially the entire reactor

length in the reactor volume, i.e. in such a way that the annular gap broadens in the direction of flow traversal.

5 The proportion of the constituent (A) in the subject coating material may vary very widely and is guided in particular by the intended flexibility of the subject sol-gel coating produced therefrom. There is an upper limit on the proportion; thus, it may not be chosen so
10 high that phase separation occurs in the subject coating material, or the hardness and mar resistance of the sol-gel coating decrease too sharply. The skilled worker is therefore able to determine the proportion which is optimal in each case, on the basis of his or
15 her knowledge in the art, with or without the assistance of simple preliminary tests.

The further essential constituent of the subject coating material is the stock coating material (B). It
20 too is preferably free of aromatic solvents.

It is produced by controlled hydrolysis and condensation of at least one organically modified hydrolyzable silane (B1). It is of advantage according
25 to the invention to use at least two silanes (B1).

The hydrolyzable silane (B1) comprises compounds of the general formula I

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where the R radicals can be identical or different and are selected from hydrolyzable groups, hydroxyl groups
5 and nonhydrolyzable groups.

The nonhydrolyzable groups R in the general formula I are preferably selected from alkyl groups, especially of 1 to 4 carbon atoms, for example methyl, ethyl,
10 propyl and butyl groups; alkenyl groups, especially of 2 to 4 carbon atoms, for example vinyl, 1-propenyl, 2-propenyl and butenyl groups; alkynyl groups, especially of 2 to 4 carbon atoms such as acetylenyl and propargyl groups; and aryl groups, especially of 6
15 to 10 carbon atoms, for example phenyl and naphthyl groups. Nonhydrolyzable groups R used are preferably alkyl groups.

Examples of hydrolyzable groups R in the aforementioned
20 formula I are hydrogen atoms; alkoxy groups, especially of 1 to 20 carbon atoms, for example methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, tert-butoxy and sec-butoxy groups; alkoxy-substituted alkoxy groups, for example beta-methoxyethoxy groups; acyloxy groups,
25 especially of 1 to 4 carbon atoms, for example acetoxy and propionyloxy groups; and alkylcarbonyl groups such as for example acetyl groups.

Particularly preferred hydrolyzable groups R are those

which bear no substituents and lead to aromatics-free hydrolysis products having a low molecular weight, for example lower alcohols, such as methanol, ethanol, propanol, n-butanol, i-butanol, sec-butanol and
5 tert-butanol.

At least one group R of the formula I shall be a hydrolyzable group. Silanes (B1) with two, preferably four and especially three hydrolyzable groups R are
10 particularly preferred.

The nonhydrolyzable groups R of the silanes (B1) may contain at least one functional group. These functional groups may be for example epoxide groups, amino groups,
15 olefinically unsaturated groups such as vinyl or (meth)acryloyl groups, mercapto groups, isocyanate groups and/or their reaction products with further reactive compounds.

20 Examples of hydrolyzable silanes (B1) particularly useful for the purposes of the invention are methyltriethoxysilane, methyltrimethoxysilane, tetramethyl orthosilicate, tetraethyl orthosilicate, 3-glycidyloxypropyltrimethoxysilane or 3-aminopropyl-
25 triethoxysilane.

The silanes (B1) can be used in whole or in part in the form of precondensates, i.e., compounds formed by partial hydrolysis of the silanes (B1), either alone or

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mixed with other hydrolyzable compounds.

The hydrolysis and condensation may optionally be carried out in the presence of organic monomers, of solvents, preferably aromatics-free solvents, of the hereinbelow described organically modified hydrolyzable metal alkoxides (C1) and of metal oxides in the form of nanoparticles.

To hydrolyze and condense the silanes (B1), a desired blend thereof is precondensed with water. The water is added at such a rate that local excess concentrations are avoided. This is accomplished for example by introducing the water into the reaction mixture using moisture-laden adsorbents, for example silica gel or molecular sieves, hydrous organic solvents, for example 80% ethanol, or salt hydrates, for example $\text{CaCl}_2 \times 6\text{H}_2\text{O}$. The precondensation is preferably effected in the presence of a hydrolysis and condensation catalyst but in the absence of an organic solvent.

In a further variant, the hydrolysis and condensation of the hydrolyzable silanes (B1) is carried out in the presence of an aromatics-free organic solvent, such as an aliphatic alcohol, such as methanol, ethanol, propanol, isopropanol or butanol, an ether, such as dimethoxyethane, an ester such as dimethylglycol acetate or methoxypropyl acetate and/or 2-ethoxyethanol or a ketone such as acetone or methyl ethyl ketone.

Optionally, the hydrolysis and condensation is carried out in the additional presence of the hereinbelow described metal alkoxides (C1) and/or metal oxides as nanoparticles.

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These nanoparticles are <50 nm. They can be for example Al_2O_3 , ZrO_2 and/or TiO_2 .

Useful hydrolysis and condensation catalysts include
10 proton- or hydroxyl-ion-detaching compounds and amines. Specific examples are organic or inorganic acids, such as hydrochloric acid, sulfuric acid, phosphoric acid, formic acid or acetic acid, and organic or inorganic bases such as ammonia, alkali metal hydroxides or
15 alkaline earth metal hydroxides, e.g., sodium, potassium or calcium hydroxide, and amines soluble in the reaction medium, examples being lower alkylamines or alkanolamines. Particular preference is given in this context to volatile acids and bases, especially
20 hydrochloric acid, acetic acid, ammonia and triethylamine.

The precondensation is not carried on beyond the point that the resulting stock coating material (B) loses its
25 liquid consistency.

Similarly, the fraction of the subject coating material which is attributable to the constituent (B) can vary within very wide limits and depends in particular on

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the target mar resistance and hardness for the subject sol-gel coating produced therefrom. The fraction has an upper limit; it must not be so high as to cause phase separation in the subject coating material and/or excessive hardness and brittleness for the subject sol-gel coatings produced therewith. The skilled worker is therefore able to determine the best fraction in each case on the basis of his or her expertise with or without the assistance of simple preliminary tests.

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The further essential constituent of the subject coating material is the sol (C), which is preparable by hydrolysis, condensation and complexation of at least one of the hereinabove described silanes (B1) and at least one hydrolyzable metal compound (C1) of the general formula II. The sol (C) is preferably aromatics-free.

15

In the general formula II, the variable M is aluminum, titanium or zirconium, but especially aluminum. Accordingly, the index n is 3 or 4.

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In the general formula II, the variable R has the same meaning as specified hereinabove in the case of the general formula I. According to the invention, it is of advantage here for at least two, especially three hydrolyzable groups to be present in the case of aluminum and three, especially four, in the case of titanium or zirconium.

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According to the invention, the hereinabove described alkoxy groups are particularly advantageous and are therefore preferred. Very particular preference is given to sec-butyloxy groups. An example of a very particularly preferred hydrolyzable metal compound (C) is accordingly aluminum tri-sec-butoxide.

The molar ratio of metal M to silicon can vary within very wide limits and depends in particular on the target mar resistance of the subject sol-gel coatings. Generally, replacing a portion of the silicon with aluminum in particular will enhance the mar resistance and the hardness of the subject sol-gel coatings. More particularly, the molar ratio M:Si is in the range from 1:10 to 1:1.5, preferably in the range from 1:6 to 1:3.

The hereinabove described silanes (B1) and metal compounds (C1) are hydrolyzed and condensed according to the invention in the presence of at least one organic, preferably nonaromatic, compound capable of forming chelate ligands. Concerned are organic compounds having at least two functional groups capable of coordinating onto metal atoms or ions. These functional groups are customarily electron donors which offer up electrons to metal atoms or ions as electron acceptors. According to the invention, in principle all organic compounds of the type mentioned are suitable, provided they do not adversely affect or even completely prevent the hydrolysis and condensation

and/or the crosslinking to the ready produced sol-gel coating. Examples of suitable organic compounds are compounds containing carbonyl groups in the 1,3 position, such as acetylacetone or ethyl acetate.

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The hydrolysis, condensation and complexation is effected substantially under the conditions specified hereinabove for the production of the stock coating material (B). More particularly, the silanes (B1),
10 metal compounds (C1) and the organic compounds capable of forming chelates are initially charged, whereupon the mixture is admixed, preferably at lower temperatures, especially 0°C, with water and at least one of the hereinabove described condensation
15 catalysts. The reaction can be carried out in the presence of the hereinabove described solvents and/or nanoparticles. According to the invention, however, it is of advantage for the reaction to be carried out in the absence of these components. Since the resulting
20 sol (C) is very reactive, it is advisable to keep it at temperatures below 0°C until it is to be put to further use.

The fraction of the subject coating material which is
25 attributable to the constituent (C) can likewise vary within very wide limits and depends in particular on how the performance profile with regard to mar resistance and hardness on the one hand and flexibility on the other is to be balanced out for the subject sol-

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gel coating produced therefrom. This fraction too has an upper limit; it must not be so high as to cause phase separation in the subject coating material and/or excessive hardness and brittleness for the subject sol-gel coatings produced therewith. The skilled worker is therefore able to determine the best fraction in each case on the basis of his or her expertise with or without the assistance of simple preliminary tests.

10 Particularly advantageous subject coating materials contain, in each case based on their total amount, 5 to 40, preferably 10 to 35 and especially 15 to 30 weight % of the acrylate copolymer solution (A), 5 to 40, preferably 10 to 35 and especially 15 to 30 weight % of
15 the stock coating material (B) and also 1 to 15, preferably 2 to 10 and especially 3 to 8 weight % of the sol (C).

It is of very particular advantage in this context, in
20 accordance with the invention, for the solids contents of the essential constituents (A), (B) and (C) to be chosen so that they are in a weight ratio of (A):(B):(C) of

- 25 - 0.5 to 5:1 to 10:1,
- preferably 1 to 4:2 to 8:1 and
- especially 1.5 to 3:3 to 6:1.

The subject coating material may further contain an additive solution (D). It is preferably aromatics-free.

The additive solution (D) contains at least one
5 ethylenically unsaturated compound (d1) which has at least one epoxide group. An example of a suitable compound (d1) is glycidyl (meth)acrylate.

It further contains as component (d2) at least one
10 silane (B1) having at least one nonhydrolyzable group R which contains at least one epoxide group. An example of a suitable compound (d2) is 3-glycidyloxypropyltri-methoxysilane.

Not least, it contains at least one adduct (d3) of at
15 least one silane (B1) with at least one nonhydrolyzable group R which has at least one amino group and with at least one cyclic ethylenically unsaturated dicarboxylic anhydride. An example of a suitable silane (B1) is 3-aminopropyltriethoxysilane. Examples of suitable
20 dicarboxylic anhydrides are maleic anhydride and itaconic anhydride.

The additive solution contains the components (d1), (d2) and (d3) in a weight ratio of (1 to 10):(1 to
25 30):1, especially (2 to 6):(10 to 20):1. The solids content of the additive solution (D) is preferably below 80 weight %, preferably below 60 weight % and especially below 50 weight %.

30 The fraction of the subject coating material which is

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attributable to the additive solution (D) can vary within wide limits, if the additive solution (D) is used. The skilled worker can determine whichever is the best fraction on the basis of his or her expertise with or without the assistance of simple preliminary tests.

The subject coating material can further contain major amounts of solvents, preferably aromatics-free solvents, as constituent (E). This is the case especially which particularly thin subject sol-gel coatings, preferably having a dry film thickness $<5 \mu\text{m}$, are to be produced. Examples of suitable solvents (E) are the hereinabove mentioned lower alcohols, especially ethanol, or glycol ethers such as ethylglycol or butylglycol.

The subject coating material can further contain customary known coating additives (F). All coating additives (F) are suitable which do not adversely affect, but advantageously vary and improve the properties profile of the subject sol-gel coatings, especially their optical properties (appearance) and mar resistance.

Examples of suitable coating additives (F) are

- UV absorbers;
- free radical scavengers;

- catalyts for crosslinking;
- slip additives;
- 5 - polymerization inhibitors;
- defoamers;
- antipopping agents, in regard to which the
10 controlled use of minor amounts of aromatic
solvents may be of benefit;
- emulsifiers, especially nonionic emulsifiers such
as alkoxyated alkanols and polyols, phenols and
alkylphenols or anionic emulsifiers such as alkali
15 metal salts or ammonium salts of alkanecarboxylic
acids, alkanesulfonic acids and sulfonic acids of
alkoxyated alkanols and polyols, phenols and
alkylphenols;
- 20 - wetting agents such as siloxanes, fluorous
compounds, carboxylic monoesters, phosphoric
esters, polyacrylic acids and their copolymers or
polyurethanes;
- 25 - adhesion promoters;
- flow control agents;
- film-forming auxiliaries such as cellulose

derivatives;

- flame retardants or
- 5 - rheology control additives such as those known from the patent documents WO 94/22968, EP-A-0 276 501, EP-A-0 249 201 or WO 97/12945; crosslinked polymeric microparticles, as disclosed for example in EP-A-0 008 127; inorganic
10 phyllosilicates such as aluminum-magnesium silicates, sodium-magnesium and sodium-magnesium-fluorine-lithium phyllosilicates of the montmorillonite type; silicas such as Aerosils; or
15 synthetic polymers having ionic and/or associative groups such as polyvinyl alcohol, poly(meth)acrylamide, poly(meth)acrylic acid, polyvinylpyrrolidone, styrene-maleic anhydride or ethylene-maleic anhydride copolymers and their derivatives
20 or hydrophobic modified ethoxylated urethanes or polyacrylates.

Further examples of suitable coating additives (F) are described in the textbook Lackadditive by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998.

25

The subject coating material has a solids content of up to 80, preferably up to 60, particularly preferably up to 40 and especially up to 20 weight %. When particularly thin subject sol-gel coatings, i.e.

5 The production of the subject coating material has no particular features, but is effected in conventional and known manner by mixing its essential constituents (A), (B) and (C) and also optionally (D), (E) and/or (F) in customary and known mixing assemblies such as
10 dissolvers. The constituents can be mixed with each other in any desired manner. For example, they can be introduced into the mixing assembly all at once. According to the invention, however, it is advantageous to initially charge the sol (C) and then to add the
15 remaining constituents one by one in succession. It is advantageous in this process to add the stock coating material (B) before the acrylate copolymer solution (A). When a solvent (E) is used, it is advantageously added after the addition of the stock coating solution
20 (B) and before the addition of the constituent (A) and optionally (D). When coating additives (F) are used, they are advantageously added after the addition of the stock coating solution (B) and before the addition of the constituent (A). When solvents (E) and coating
25 additives (F) are used, the coating additives (F) are added before the addition of the solvents (E).

The subject coating materials are very useful for producing the subject sol-gel coatings, especially sol-

gel clearcoat materials.

According to the invention, any conceivable substrate can be coated therewith. By way of example, mention may
5 be made of substrates of metal, plastic, glass, wood or ceramic. These substrates may have been primed. In the case of plastic, the priming may take the form of hydropriming. In the case of metal, the substrate may also have been subjected to a surface treatment such as
10 galvanizing or phosphating or anodizing for example. Furthermore, the metal substrate may already support an electrocoat and a surfacer as priming.

The application of the subject coating materials has no
15 special process features, and the customary application methods such as spraying, knife coating, spread coating, casting, dipping or rolling can be used.

After application, the subject coating materials are
20 cured to form the subject sol-gel coating. Curing may be preceded by a predrying step. Again the customary and known processes and apparatuses such as through air ovens can be used. According to the invention, however, it is of advantage to cure the subject coating
25 materials with intermediate IR radiation. This makes it possible to specifically coat and make mar resistant only parts of substrates or single-coat or multicoat paint systems at damaged or at particularly vulnerable points without the other parts being exposed to thermal

stress. This enables the subject coating materials to be used in automotive repair finishing. Since here, moreover, the amount of the subject coating material can be restricted to a minimum, its use is also particularly economical.

The subject coating materials can be applied directly to the substrates in order that a mar resistant subject sol-gel coating may be formed thereon after curing. In this way it is possible to obtain mar resistant finishes on substrates as are customary for the manufacture of vehicles, of other structural parts and equipment, such as radiators or containers, or of furniture.

However, the particular advantages of the subject coating materials become particularly evident when they are used for coating single-coat or multicoat paint systems with the subject sol-gel coatings. It proves to be a particular advantage here that the single-coat or multicoat paint systems may have been completely cured.

Accordingly, the subject coating materials are useful for coating single-coat or multicoat paint systems of the type customary and known in the fields of automotive original equipment manufacturing coatings, automotive repair coatings, industrial coatings, including container coatings, plastics coatings and furniture coatings.

Examples of single-coat paint systems of this kind are the solid shade topcoats known in automotive original equipment manufacturing finishing, which contain binders, crosslinkers and effect- and/or color-
5 conferring pigments.

Examples of multicoat paint systems are those which contain an effect- and/or color-conferring basecoat, especially a waterborne basecoat, and a clearcoat and
10 are generated in the realm of automotive original equipment manufacturing coating by the wet on wet process as described for example in the patent documents US-A-3,639,147, DE-A-33 33 072, DE-A-38 14 853, GB-A-2 012 191, US-A-3,953,644,
15 EP-A-0 260 447, DE-A-39 03 804, EP-A-0 320 552, DE-A-36 28 124, US-A-4,719,132, EP-A-0 297 576, EP-A-0 069 936, EP-A-0 089 497, EP-A-0 195 931, EP-A-0 228 003, EP-A-0 038 127 and DE-A-28 18 100, or in the realm of automotive repair finishing. The
20 subject coating materials are particularly useful for coating multicoat paint systems of this kind in particular.

Examples of suitable waterborne basecoats and of
25 corresponding multicoat paint systems are known from the patent documents EP-A-0 089 497, EP-A-0 256 540, EP-A-0 260 447, EP-A-0 297 576, WO 96/12747, EP-A-0 523 610, EP-A-0 228 003, EP-A-0 397 806, EP-A-0 574 417, EP-A-0 531 510, EP-A-0 581 211,

- EP-A-0 708 788, EP-A-0 593 454, DE-A-43 28 092,
EP-A-0 299 148, EP-A-0 394 737, EP-A-0 590 484,
EP-A-0 234 362, EP-A-0 234 361, EP-A-0 543 817,
WO 95/14721, EP-A-0 521 928, EP-A-0 522 420,
5 EP-A-0 522 419, EP-A-0 649 865, EP-A-0 536 712,
EP-A-0 596 460, EP-A-0 596 461, EP-A-0 584 818,
EP-A-0 669 356, EP-A-0 634 431, EP-A-0 678 536,
EP-A-0 354 261, EP-A-0 424 705, WO 97/49745,
WO 97/49747 or EP-A-0 401 565.
- 10 Examples of suitable one component, two component or
multicomponent (three component, four component)
clearcoat materials are known for example from the
patent documents DE-A-42 04 518, US-A-5,474,811,
US-A-5,356,669, US-A-5,605,965, WO 94/10211,
15 WO 94/10212, WO 94/10213, EP-A-0 594 068,
EP-A-0 594 071, EP-A-0 594 142, EP-A-0 604 992,
WO 94/22969, EP-A-0 596 460 or WO 92/22615.

One component clearcoat materials, as will be known,
20 contain hydroxyl-containing binders and crosslinkers
such as blocked polyisocyanates, tris(alkoxycarbonyl-
amino)triazines and/or aminoplast resins. In a further
variant they contain polymers having pendant carbamate
and/or allophanate groups as binders and optionally
25 carbamate- and/or allophanate-modified aminoplast
resins as crosslinkers.

Two-component or multicomponent (three component, four
component) clearcoat materials, as will be known,

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contain hydroxyl-containing binders and polyisocyanate crosslinkers as essential constituents, which have to be kept separated before use.

5 Examples of suitable powder clearcoat materials are known for example from the German patent document DE-A-42 22 194 or BASF Lacke + Farben AG's 1990 Pulverlacke product information bulletin.

10 Powder clearcoat materials, as will be known, contain epoxy-containing binders and polycarboxylic acid crosslinkers as essential constituents.

Examples of suitable powder slurry clearcoat materials
15 are known from the US patent US-A-4,268,542 and the
German patent applications DE-A-195 18 392.4 and
DE-A-196 13 547 or are described in the German patent
application DE-A-198 14 471.7, which was unpublished at
the priority date of the present invention.

20

Powder slurry clearcoat materials, as will be known, contain powder clearcoat materials dispersed in an aqueous medium.

25 UV curable clearcoat materials are disclosed for
example in the patent documents EP-A-0 540 884,
EP-A-0 568 967 or US-A-4,675,234.

As will be known, they contain actinically and/or

electron beam curable low molecular weight, oligomeric and/or polymeric compounds, preferably radiation curable binders, especially on the basis of ethylenically unsaturated prepolymers and/or ethylenically unsaturated oligomers, optionally one or more reactive diluents and also optionally one or more photoinitiators. Examples of suitable radiation curable binders are (meth)acryloyl-functional (meth)acryloyl copolymers, polyether acrylates, polyester acrylates, unsaturated polyesters, epoxy acrylates, urethane acrylates, amino acrylates, melamine acrylates, silicone acrylates and the corresponding methacrylates. Preference is given to using binders which are free of aromatic structural units.

However, it is also possible to employ multicoat clearcoat systems such as for example a clearcoat system based on hydroxyl-containing binders and blocked polyisocyanates and aminoplasts as crosslinkers, which is situated directly atop the waterborne basecoat and on top of which there is a further clearcoat based on carbamate and/or allophanate group containing binders and aminoplasts as crosslinkers.

In the subject process, the single-coat or multicoat paint systems, especially the clearcoats, are cured prior to application of the subject coating material. This constitutes a further particular advantage of the subject coating material and of the process, since the coating processes and apparatuses customarily used in

commercial practice do not have to be modified; all that is needed is that a customary known process is followed by a further coating step which is essentially independent thereof.

5

It proves to be a further particular advantage that substantially all customarily used clearcoat systems can be coated with the subject coating material.

10 The subject sol-gel coatings which are produced from the subject coating materials, preferably by the subject process, are notable for excellent mar resistance coupled with very good adhesion, even after exposure to condensation. Similarly, the appearance is
15 very good. The subject process is therefore particularly useful for the coating of vehicle bodies, especially automobile bodies, with multicoat systems; for industrial coating, including coil coatings, plastics coating and furniture coating.

20

Examples

Preparation Example

25 **Preparation of subject sol-gel clearcoat material**

1. Preparation of a stock coating material

30 parts of completely ion-free water, 40 parts of
30 ethylglycol, 5 parts of acetic acid (100%), 66.5 parts

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of methyltriethoxysilane and 4.7 parts of 3-glycidyl-
oxypropyltrimethoxysilane were charged under nitrogen
to a suitable reaction vessel and heated to 60°C with
stirring. Following a further 3 hours at 60°C, the
5 stirred reaction mixture was heated to 90°C and
maintained at 90°C for 2 hours. 70 parts of the
reaction mixture were then distilled off azeotropically
at 85°C. After cooling to room temperature, the
reaction mixture was admixed with 5 parts of
10 methoxypropyl acetate and 0.1 part of BYK® 301 (flow
control agent from BYK). The result was stock coating
material 1 having a theoretical solids content of 37%
by weight and an experimentally determined solids
content of 45% by weight (1 hour/130°C).

15

2. Preparation of an acrylate copolymer for modifying the sol-gel clearcoat material

39 parts of ethoxyethyl propionate were charged to a
20 suitable stirred vessel equipped with reflux condenser
and stirrer and were heated to 130°C. A first monomer
feed vessel was used to premix 9.598 parts of butyl
methacrylate, 7.708 parts of methyl methacrylate,
8.003 parts of styrene, 4.253 parts of Methacrylester
25 13.0 (methacrylic ester having a long alkyl radical in
the ester moiety) and 9.096 parts of hydroxyethyl
acrylate. A second monomer feed vessel was charged with
3.810 parts of hydroxyethyl acrylate, 1.831 parts of
acrylic acid and 0.916 part of ethoxyethyl propionate.

An initiator feed vessel was charged with 3.692 parts of TBPEH (tert-butyl perethylhexanoate) peroxide and 6.025 parts of ethoxyethyl propionate. The contents of the first monomer feed vessel were metered into the reactor at a uniform rate over four hours. After two hours and 30 minutes after the start of the first monomer feed, the second monomer feed was started. To this end, the contents of the second monomer feed were metered into the reactor at a uniform rate over one hour and 30 minutes. The contents of the initiator feed vessel were metered into the reactor at a uniform rate over four hours and 30 minutes, the start of the initiator feed being started five minutes before the first monomer feed. After the additions, the resulting reaction mixture was polymerized at 130°C for two hours until an original viscosity of 2.2 dPas, a solids content of 50% by weight (15 minutes/180°C) and an acid number of 30 mg of KOH/g have been obtained. Thereafter, the ethoxyethyl propionate was distilled off at 100°C under reduced pressure until a solids content of 81% by weight was reached. The resulting reaction mixture was cooled to 80°C and adjusted to a solids content of 75% by weight with butylglycol and ethoxyethyl propionate (weight ratio 5:1).

25

To prepare the subject sol-gel clearcoat material, the solution of the acrylate copolymer was adjusted to a solids content of 20% by weight with butylglycol to obtain the solution for the organic modification 2.

3. Preparation of a sol to be used according to the invention

5 A mixture of 138.6 parts of aluminum tri-sec-butoxide, 178.3 parts of methyltriethoxysilane, 401.78 parts of 3-glycidyloxypropyltrimethoxysilane and 82.6 parts of ethyl acetate was charged to a suitable reaction vessel at 0°C. 198.72 parts of 0.1 N hydrochloric acid were metered into the initial charge at 0°C. After addition, 10 the resulting reaction mixture was aged at room temperature for 24 hours. Assuming 100% conversion, the theoretical solids content was 37.88% by weight and the theoretical solvent content 53.11% by weight. The experimentally determined solids content was 44.6% by 15 weight (15 minutes/180°C). The pH of the Ormocer solution was 3.1. The viscosity (original) was 20 mPas at a shear gradient $D = 103 \text{ s}^{-1}$. The sol was kept at -18°C until used for preparing the subject sol-gel clearcoat material.

20

4. Preparation of the subject sol-gel clearcoat material

25 The sol-gel clearcoat material 4 was obtained by initially charging 9.81 parts of the sol 3 and adding to it in succession 35.8 parts of the stock coating material 1 (45% by weight in ethylglycol), 0.2 parts of BYK® 301, 65 parts of ethanol and 40 parts of the solution for organic modification 2 with stirring and

mixing the constituents. The result was the subject sol-gel clearcoat material 4 having a solids content of 19% by weight.

5 **Example**

1. **Preparation of a subject sol-gel coating on a multicoat paint system**

10 A commercially available surfacer from BASF Coatings AG was applied with a cup gun to steel panels cathodically coated to a depth of 18-22 μm with a commercially available electrocoat material and baked in. The result was a surfacer coat 35 to 40 μm in thickness. A
15 commercially available black solid shade basecoat material from BASF Coatings AG was then applied atop the surfacer in the same way and predried at 80°C for 10 min. After cooling the panels, a coat of a commercially available two component clearcoat material
20 (FF98-0015 from BASF Coatings AG) was applied and predried at 50°C for 10 min and then crosslinked at 140°C together with the basecoat for 45 min. The result was a basecoat 15 μm in thickness and a clearcoat 44 μm in thickness. The black solid shade basecoat material
25 was chosen because any marring is most easily detectable on the corresponding test panels.

After cooling, the subject sol-gel clearcoat material 4 of the preparation example was applied, so that the

subject sol-gel coating was obtained in a thickness of 4.5 μm after curing with intermediate IR radiation (distance of radiator from surface 18 cm; radiator: Modul Infrarotstrahler MMS 2000 from Haraeus).

5

2. Testing of the properties of the subject sol-gel coating

2.1 Adhesion of the sol-gel coating

10

Table 1 gives an overview of the mechanical tests and of the results obtained.

Table 1:

15

Adhesion of subject sol-gel coating

Test methods	Example
---------------------	----------------

Mar test DBL 7399 [rated from 0 to 5]	0
---------------------------------------	---

Mar test after 240 hours of constant condensation conditions (CCC) [rated from 0 to 5]	0
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Cross-hatch to DIN 53151 (2 mm) [rated from 0 to 5]	0
--	---

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Cross-hatch after 240 hours of CCC and
24 hours of regeneration

0

[rated from 0 to 5]; 0 = best value; 5 = worst value

Although the clearcoat had been completely baked prior
5 to its overcoating with the sol-gel coating, there was
no delamination of the sol-gel coating.

2.2 Mar resistance of the sol-gel coating by the brush test

10

Before this test was carried out, the test panels were
aged at room temperature for at least 2 weeks following
application of the coatings.

15 The mar resistance of the sol-gel coating on the test
panels was assessed with the aid of the BASF brush test
described in Fig. 2 on page 28 of the article by
P. Betz and A. Bartelt, Progress in Organic Coatings,
22 (1993), pages 27 -37, albeit with modification with
20 regard to the weight used (2 000 g instead of the 280 g
mentioned therein), assessment taking place as follows:

In the test, the surface of the paintwork was damaged
with a mesh fabric loaded with a mass. The mesh fabric
25 and the paintwork surface were copiously wetted with a
laundry detergent solution. The test panel was moved to

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and fro underneath the mesh fabric in reciprocal movements by means of a motor drive.

Test element was an eraser (4.5 × 2.0 cm, broad side
5 perpendicular to the direction of marring) covered with
nylon mesh fabric (No. 11, 31 μ m mesh size, Tg 50°C).
The applied weight was 2 000 g.

Prior to each test, the mesh fabric was renewed, with
10 the running direction of the fabric meshes parallel to
the direction of marring. Using a pipette, about 1 ml
of a freshly stirred 0.25% strength Persil solution was
applied in front of the eraser. The rotary speed of the
motor was adjusted so that 80 double strokes were
15 performed within a period of 80 s. After the test, the
remaining wash liquor was rinsed off with cold tap
water and the test panel was blown dry with compressed
air.

20 It was found that the subject sol-gel coatings were
completely free of any marring.

2. Surface slip of subject sol-gel coating

25 The surface slip was measured using the MOD 9505AE -
SERIAL 7035-0689-2 slip meter from ALTEK, P.O. Box
1128, Torrington, Connecticut 06790, USA. In this
measurement, a weight provided with three hemispheres
was pulled with a constant force over the surface of

the test panels. The frictional resistance which occurred when this done was plotted graphically as a dimensionless variable using an x/y plotter. The height of the resultant peak is a relative measure of the lubricity of the surface in question: the lower the height, the more lubricious the surface.

In this test, the sol-gel coating had a relative peak height of 0.06. For comparison, the commercially customary two component clearcoat material (FF98-0015 from BASF Coatings AG) used to produce the multicoat system had a relative peak height of 0.05.

2.4 Chemical resistance

2.4.1 Chemical resistance by the MB gradient oven test

In the well-known MB gradient oven test, the test panels of the example were exposed under defined condition to damage by sulfuric acid, water, pancreatin and tree resin. For this purpose, the test substances were applied at a distance of one segment width in each case (adjustment of the gradient to 30 - 75°C [1°C per heating segment]). Following storage under standard conditions 23°C for 72 hours, the test panels were exposed for 30 min in a gradient oven (e.g. type 2615 from BYK-Gardner). The temperature at which the first visible change occurred was determined.

The experimental results are reported in Table 2.

Table 2: Chemical resistance by the MB gradient oven test

Test substance	Example 1st marking at °C
Sulfuric acid 1%	54
Water distilled	>75
Pancreatin	48
Tree resin	>75

- 5 The results of the MB gradient oven test substantiate the high chemical resistance of the subject sol-gel coating.

2.4.2 Resistance to dishwasher detergent

10

This test was carried out using a dishwasher detergent having a pH of 10.8. The test panels were exposed to the amounts of detergent reported in Table 3, in the reported concentrations, at 23°C (conditioning cabinet) or 30°C (through air oven) for 30 minutes. The resulting damage was in each case rated as follows:

15

Rating	Meaning
0	no damage
1	slight discoloration
5 2	discoloration
3	edge marking

Table 3 gives an overview of the results obtained.

10 **Table 3: Resistance of subject sol-gel coating to dishwasher detergent**

Amount of detergent (ml)	Temperature (°C)	Concentration	
		1%	5%
0.025	23	0	0
0.8025	30	1	1
0.05	30	0	0
0.075	30	0	0
0.1	30	0	0
0.125	30	0	0

The values of Table 3 substantiate the high chemical stability of the subject sol-gel coating.

2.5 Stone chipping test

AUDI AG's well-known stonechip test under multiple impact (2x500 gram/2 bar) yielded an index of 3 and a degree of rusting of 2. The subject sol-gel coating together with the multicoat paint system accordingly proved to be sufficiently stable to stone chipping.

2.6 Erichsen indentation

10

The Erichsen indentation to DIN EN ISO 1520: 1995-04 was 0.9 mm.

2.7 Appearance

15

2.7.1 Waviness

The waviness of the subject sol-gel coating was measured by wave scan. For this purpose, a laser beam was directed at the surface at an angle of 60° and the fluctuations of the reflected light were recorded over a stretch of 10 cm.

A value of 8.0 was found in the longwave range (0.6 to 10 mm; observer's distance: 2.5 m). There were accordingly no orange peel structures or other defects in the paintwork.

A value of 27.9 was found in the shortwave range (0.1

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to 0.6 mm; observer's distance: 45 cm). Accordingly, only few if any fine structures of this order of magnitude were present in the surface.

5 **2.7.2 Gloss and haze**

Gloss and haze were measured reflectometrically at an angle of 20° using a BYK reflectometer. The subject sol-gel coating had a gloss of 75 and a haze of 23 and
10 hence was in accord with commercial requirements in this respect as well.

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Claims

1. A sol-gel coating material comprising

5 (A) an acrylate copolymer solution comprising at least one acrylate copolymer (A1) preparable by copolymerizing at least the following monomers:

10 a1) at least one (meth)acrylic ester which is substantially free of acid groups,

15 a2) at least one ethylenically unsaturated monomer which bears at least one hydroxyl group per molecule and is substantially free of acid groups, and

20 a3) at least one ethylenically unsaturated monomer which bears per molecule at least one acid group which is convertible to the corresponding acid anion group;

25 (B) a stock coating material preparable by hydrolyzing and condensing at least one hydrolyzable silane (B1) of the general formula I



where the variable R has the following meaning:

R = hydrolyzable groups, hydroxyl groups and nonhydrolyzable groups with the proviso that there is at least one and there are preferably at least two hydrolyzable group(s);

and

(C) a sol preparable by hydrolyzing, condensing and complexing at least one hydrolyzable silane (B1) of the general formula I and at least one hydrolyzable metal compound (C1) of the general formula II



where the variables and the index have the following meaning:

M = aluminum, titanium or zirconium,

R = hydrolyzable groups, hydroxyl groups and nonhydrolyzable groups with the proviso that there is at least one and there are preferably

at least two hydrolyzable
group(s), and

n = 3 or 4.

5

2. The sol-gel coating material of claim 1,
characterized in that it is aromatics free.

10

3. The sol-gel coating material of claim 1 or 2,
characterized in that it comprises, in each case
based on its total amount, 5 to 40, preferably 10
to 35 and especially 15 to 30 weight % of the
acrylate copolymer solution (A), 5 to 40,
preferably 10 to 35 and especially 15 to
15 30 weight % of the stock coating material (B) and
also 1 to 15, preferably 2 to 10 and especially 3
to 8 weight % of the sol (C).

20

4. The sol-gel coating material of any of claims 1 to
3, characterized in that the solids contents of
the constituents (A), (B) and (C) are in a weight
ratio of (A):(B):(C) of

25

- 0.5 to 5:1 to 10:1,
- preferably 1 to 4:2 to 8:1 and
- especially 1.5 to 3:3 to 6:1.

5. The sol-gel coating material of any of claims 1 to 4, characterized in that

- the nonhydrolyzable groups R are alkyl groups, especially of 1 to 4 carbon atoms; alkenyl groups, especially of 2 to 4 carbon atoms; alkynyl groups, especially of 2 to 4 carbon atoms; and/or aryl groups, especially of 6 to 10 carbon atoms; and

- the hydrolyzable groups R are hydrogen atoms, alkoxy groups, especially of 1 to 20 carbon atoms; alkoxy-substituted alkoxy groups of 3 to 20 carbon atoms; acyloxy groups, especially of 1 to 4 carbon atoms; alkylcarbonyl groups, especially of 2 to 6 carbon atoms.

6. The sol-gel coating material of claim 5, characterized in that

- the hydrolyzable groups R are methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, sec-butoxy, beta-methoxyethoxy, acetoxy, propionyloxy and/or acetyl groups and the

- nonhydrolyzable groups R are methyl, ethyl, propyl, butyl, vinyl, 1-propenyl, 2-propenyl,

butenyl, acetylenyl, propargyl, phenyl and/or
naphthyl groups.

7. The sol-gel coating material of any of claims 1 to
5 6, characterized in that the nonhydrolyzable
groups R contain at least one functional group,
especially at least one epoxide group, amino
group, olefinically unsaturated group, mercapto
group and/or isocyanate group and/or their
10 reaction products with further reactive compounds.
8. The sol-gel coating material of any of claims 1 to
7, characterized in that complexing is effected
using organic compounds which form chelate
15 ligands.
9. The sol-gel coating material of any of claims 1 to
8, characterized in that it is a sol-gel clearcoat
material.
- 20 10. The use of the sol-gel coating material of any of
claims 1 to 9 for producing mar-resistant sol-gel
coatings, especially for single-coat or multicoat
paint systems.
- 25 11. The use of the sol-gel coating material of claim
10, characterized in that cured single-coat or
multicoat paint systems are concerned.

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12. The use of the sol-gel coating material of claim
10 or 11, characterized in that the paint systems
are vehicle original equipment manufacturing
coatings, vehicle repair coatings, industrial
5 coatings, including container coatings, plastics
coatings and furniture coatings.
13. A process for producing mar-resistant sol-gel
coatings on single-coat or multicoat paint systems
10 by
- (i) applying a single-coat or multicoat paint
system to a primed or unprimed substrate,
 - 15 (ii) applying a sol-gel coating material atop the
single-coat or multicoat paint system and
 - (iii) curing the sol-gel coating material,
- 20 characterized in that a sol-gel coating material
as claimed in any of claims 1 to 9 is used.
14. The process of claim 13, characterized in that the
applied sol-gel coating material is cured by
25 irradiation with intermediate IR radiation.
15. The process of claim 13 or 14, characterized in
that the single-coat or multicoat paint system has
been completely cured.

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16. The process of any of claims 13 to 15,
characterized in that the paint systems are
automotive original equipment manufacturing
coatings, automotive repair coatings, industrial
5 coatings, including container coatings, plastics
coatings and furniture coatings.

17. Sol-gel coatings preparable from a sol-gel coating
material as claimed in any of claims 1 to 9 and/or
10 by the process of any of claims 13 to 16.

18. Substrates comprising at least one sol-gel coating
as claimed in claim 18.

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[illegible]

DECLARATION —

Utility or Design Patent Application

POWER OF ATTORNEY

☒ I hereby appoint the practitioner(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith application and to transact all business in the Patent and Trademark Office connected therewith

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26922

PATENT TRADEMARK OFFICE

or



Correspondence address below

County	United States of America	Telephone	(248) 948-2019	Fax	(248) 948-2093
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name OF SOLE OR FIRST NVENTOR: ☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any])		Peter		Family Name or Surname		BETZ	
Inventor's Signature		<i>P. L. Betz</i>		Date		23 06 01	
Residence: City	D-48165	State	Germany	Country	Federal Republic of Germany	Citizenship	German
	Münster	DEX					

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DECLARATION —

Utility or Design Patent Application

POWER OF ATTORNEY

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Name OF SECOND INVENTOR:

☐

A petition has been filed for this unsigned inventor

Given Name
(first and middle [if any])

Wilfried

Family Name
or Surname

STÜBBE

Inventor's
Signature

Date

07.08.01

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DECLARATION —

Utility or Design Patent Application

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Name of Additional Joint Inventor, If any:

☐ A petition has been filed for this unsigned inventorGiven Name
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Horst

Family Name
or Surname

HINTZE-BRÜNING

Inventor's
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